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High Ammonia Yield Using Magnetic Induction Method

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ACE-X 2011

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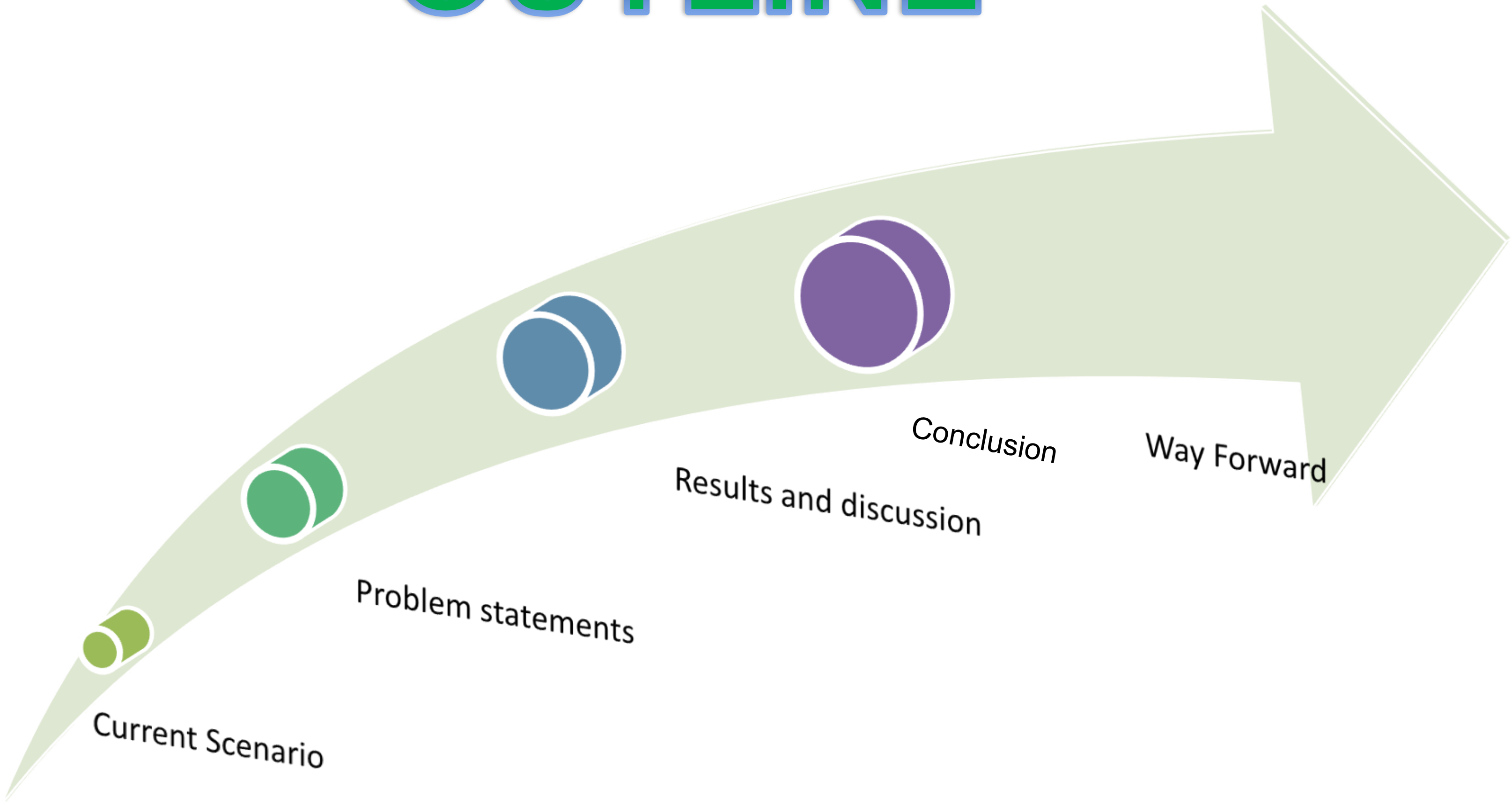
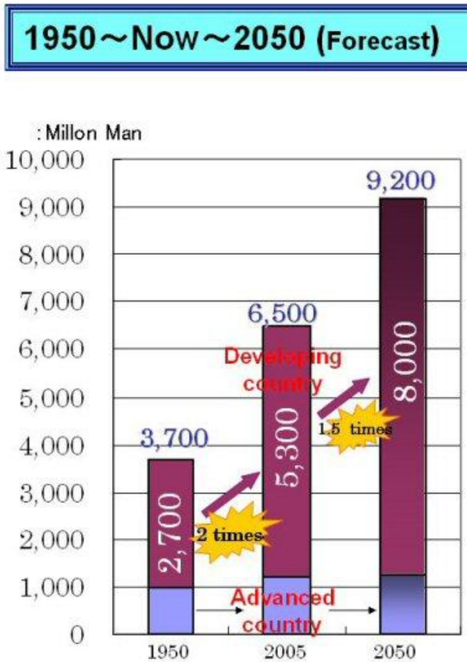
MALAYSIA

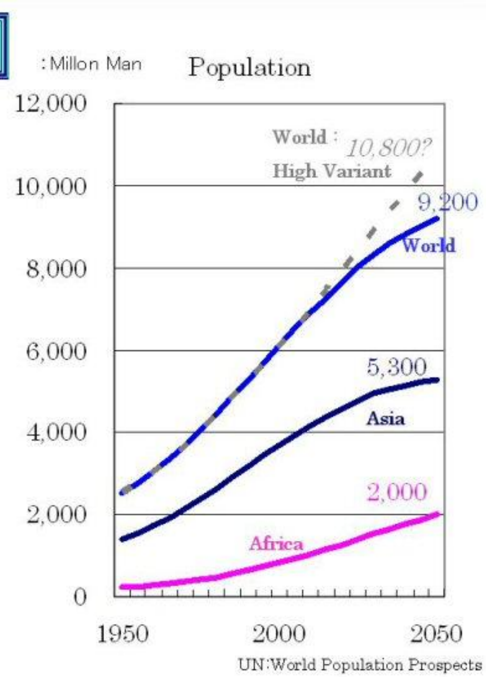
OUTLINE

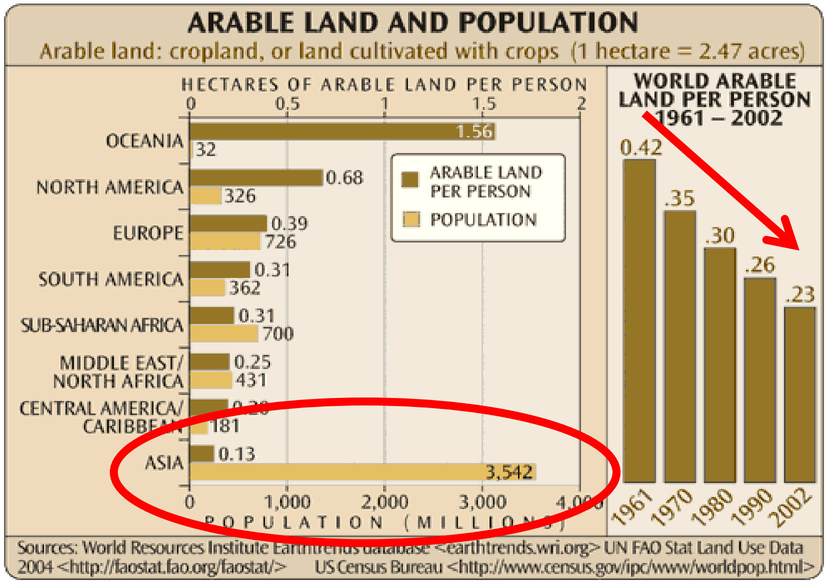


Current Scenario
Problem statements
Results and discussion
Conclusion
Way Forward

CURRENT SCENARIO







"World population is projected to grow from 6.5 billion in 2005 to nearly **9.2 billion by 2050**. To feed a population of more than 9 billion free from hunger, global food production must nearly **double by 2050.**

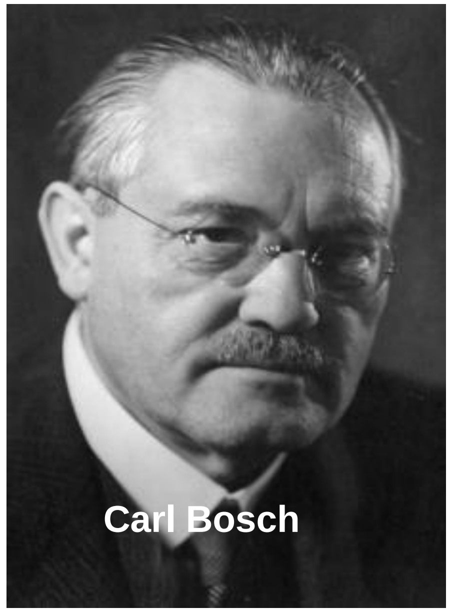
Source: Economic and social affairs, United Nation , Population Division, 2004

Arable Land is decreasing!

Need to increase agricultural efficiency

CURRENT SCENARIO

Haber-Borch Process → Synthetic Fertilizer



"Haber-Borch process (Nobel Prize-1918) was perhaps the most important invention of the twentieth century. Gunpowder and **synthetic fertilizer** for the growth of world population. Ammonia is the feedstock for urea production".

Source: *http://www.wisegeek.com*


NEW STRAITS TIMES
ESTABLISHED 1845
FRIDAY DECEMBER 18, 2009

FREE CAR AND CASH, TOO
DETAILS ON PAGE 47

Malaysia wins football gold
> P45

AirAsia, Virgin airlines in F1 honour race

Najib pledges 40pc carbon cut
'Malaysia is committed to do its best'

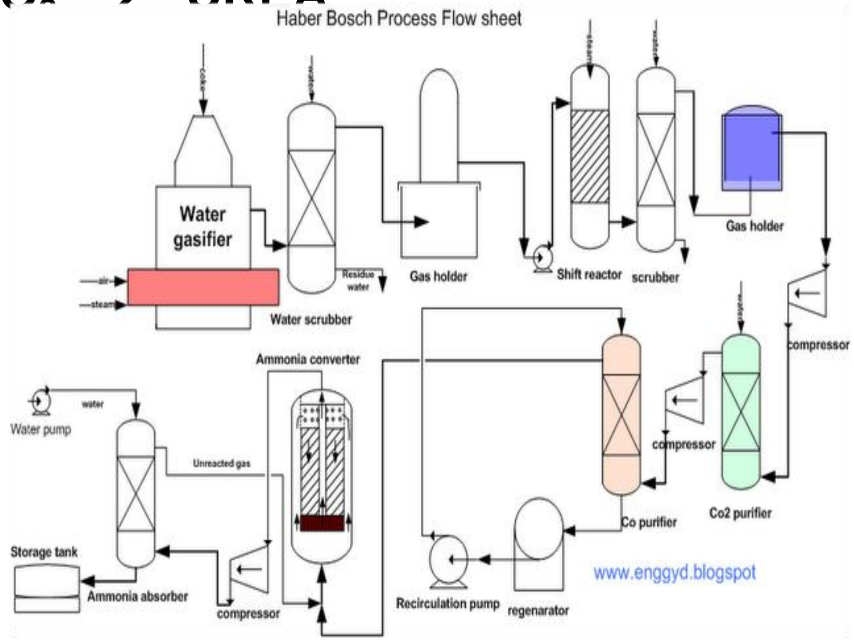
From Mimi Syed Yusof in Copenhagen

MALAYSIA will voluntarily slash by up to 40 per cent her carbon emission by 2020 compared with 2005 levels.

Kyoto Protocol: New Innovative Economic Model

CURRENT SCENARIO : AMMONIA PRODUCTION

NATURAL GAS + STEAM + AIR → $3H_2$ + CO_2 + N_2 → AMMONIA + CO_2 → UREA



Process	Pressure, atm	Temp, ^{0}C	Conversion, %
Stami Carbon	310	500	10-30
Fauster-Montecatini	220-230	500	10-30
Casale	500-700	500	15-25
Clued	330-630	540-590	15-25
Haber Bosch	**330**	**500-550**	**10-30**
Nitrogen Eng.Corp	200-300	500-550	10-30
Lummus	270-330	500-510	10-25
Kellogg	300-350	---	10-30
Du Pont	900-1000	500-600	40-80

HABER BOSCH

Pressure = 330 atm
Temperature = 500-550 ^oC
Conversion = 10 – 30%

Energy Demand = 14 – 15 GJ/ton NH_3

Energy Demand = 28-30 GJ/ton NH_3

Yahya et al., Ammonia Synthesis. Carbon and Oxide Nanostructures. Springer. Verlag (2010)

PROBLEM STATEMENTS

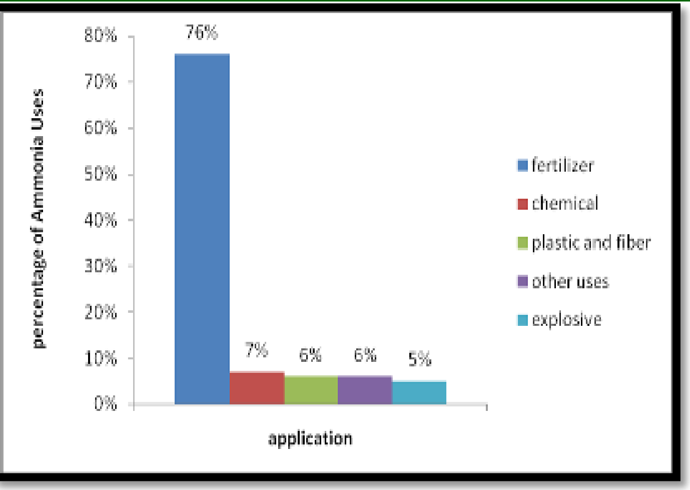
Manufacturing
Ammonia production: Energy intensive industry (pressure and temperature) Economically , Inherent to safety and global warming Ammonia yield: 18 %

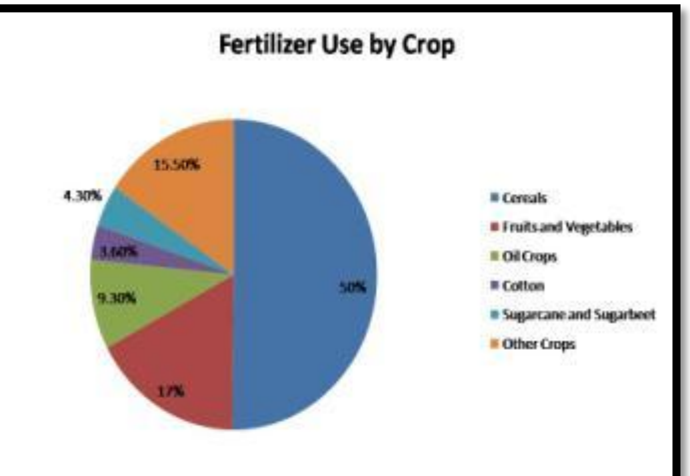
NEW ECONOMIC MODEL – HIGH INCOME COUNTRY MALAYSIA

SOLUTIONS

MANUFACTURING
Manufacturers: Greener environment and safer process High yield and efficient using green and nanotechnology

INTRODUCTION : Ammonia





- Ammonia is a chemical compound that plays an important role in our daily life.
- About 76% from the total ammonia production is been used in making fertilizer.
- Synthesizing high yield of ammonia by a process known as Haber-Bosch process still remains challenge.
- Currently by applying magnetite (Fe_3O_4) as a catalyst, the industry only capable to produce 20% maximum ammonia yield with applying high temperature and pressure that contribute to the high cost of production.

Flavia G. Duran, Bibiana P. Barbero, Luis E. Cadius, Cristina Rojas, Miguel A. Centeno, Jose A. Odrizola, Applied Catalyst B: Environmental 92, 194-201**, (2009)**

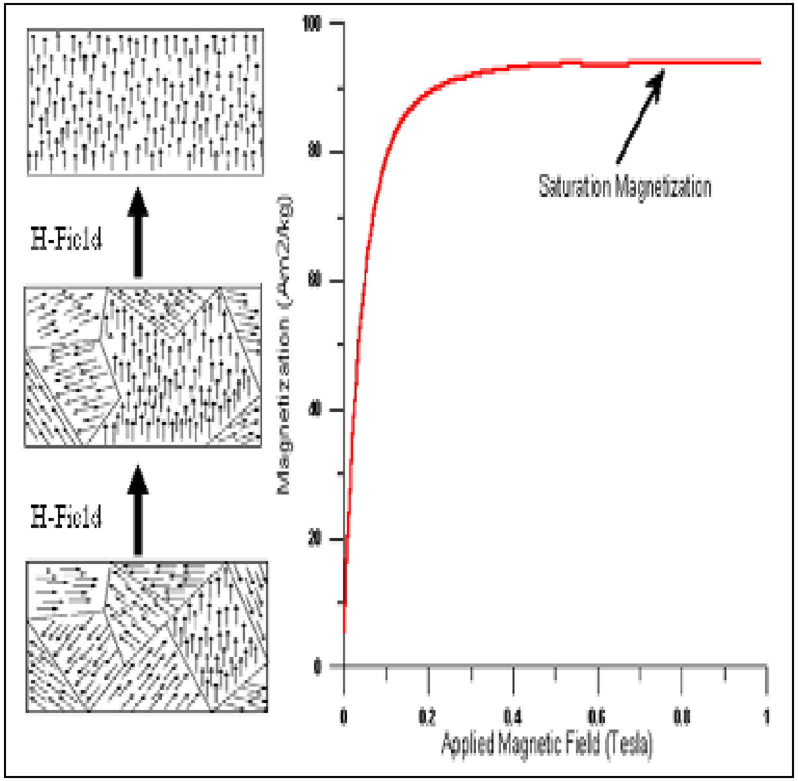
LITERATURE REVIEW

Catalysts/ Ref.	Support	Yield NH_3	Temperature	Pressure
Ruthenium [14]	Graphitised Carbon	8.5 %	400°C	63 bar
Ruthenium [15]	Graphitised Carbon	11.5 %	400°C	90 bar
Ruthenium [13]	Active carbon	40-50 %	370°C–400°C	50 – 100 atm
K-C-Fe [26]	Al_2O_3	0.48 % vol	350°C	Atm. Pressure
Wustite A301 [27]	Al_2O_3	27 % vol	425°C	15 MPa
Polyacrylonitrile (PAN) [28]	Active carbon	0.98 % vol	673 K	Atm. Pressure
$Mn_{0.8}Zn_{0.2}Fe_2O_4$ [18]	MWCNT	24.9 %	28°C	Atm. Pressure
$Mn_{0.8}Zn_{0.2}Fe_2O_4$ [10]	MWCNT	46 %	28°C	Atm. Pressure

Patent Filling	Title of Invention	Summary of Invention
4107277 [4]	Process for Production of Ammonia	Pressure condition = 200 atm, temperature condition = 80K – 360K.
4148866 [5]	Low Energy Ammonia Synthesis Process	Pressure between 20-100 atm, temperature condition = 315°C – 424°C.
4479925 [6]	Preparation of Ammonia Synthesis	Pressure condition = 25 50 bars, temperature condition = 450°C – 700°C.
4695442 [7]	Ammonia Synthesis Process	Pressure condition = 40 - 120 bar, temperature condition = 300°C – 450°C. Ratio H_2/N_2 = 2.7 to 3.0.

- Yahya et al., Journal of Nano Research. Vol. 11, 01. pp 25-34. (2010)

MAGNETISM

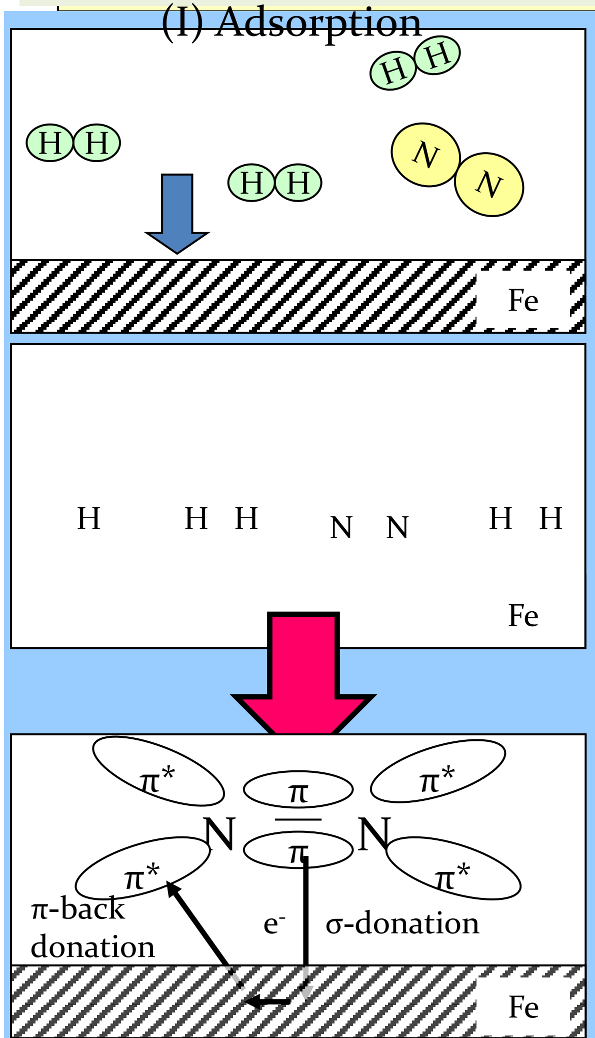


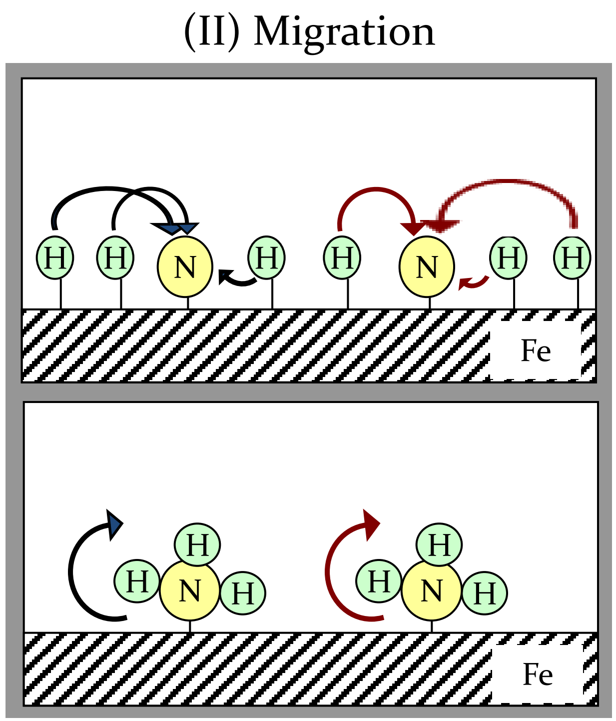
Absence of domain wall and formation of parallel aligned electrons may overcome the difficulty in exchanging/pairing of electrons among d-orbital and reactant molecules

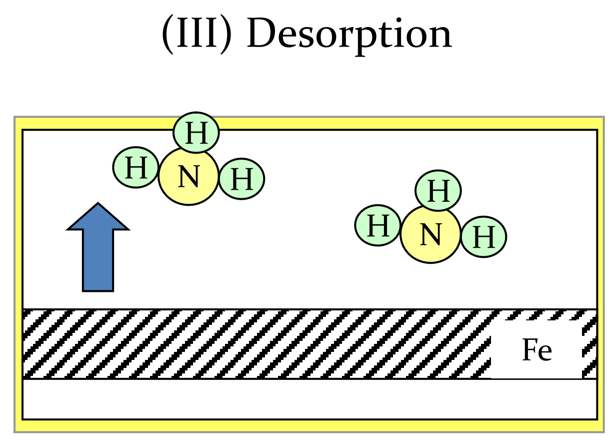
ADSORPTION - DESORPTION

CATALYST ACTIVATION

- α-Fe_2O_3 → Fe_3O_4 → $Fe_{1-x}O$ → α-Fe
- **Reduction with H_2**







Catalytic steps in ammonia synthesis.

R. S. Swathi and K. L. Sebastian, "Molecular mechanism of heterogeneous catalysis, general article: The 2007 nobel prize in chemistry," Humanities, Social Sci. and Law, vol. 13, no. 6, pp. 548-560, 2008.
J. Hagen, Industrial catalysis: A practical approach, 2nd ed., Weiheim, Germany: Wiley-Interscience,

PROMOTER

- Structural Promoter

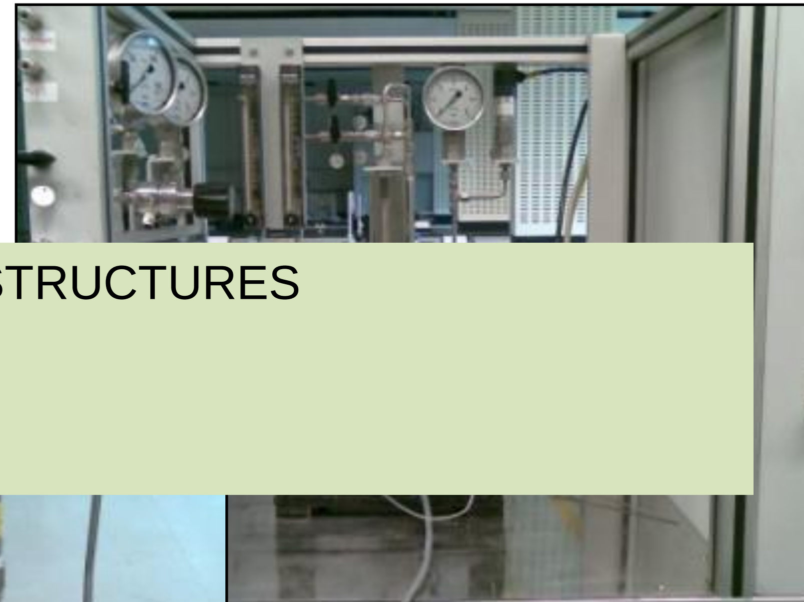
A component that can hold the particles and prevent agglomeration. Since the active phase or pure metal tends to agglomerate with neighbouring particles especially at high temperature due to high surface energy.

- Electronic Promoter

A promoter that provide excess electron to the catalyst system to enhance and accelerate the dissociation of reactant molecules.

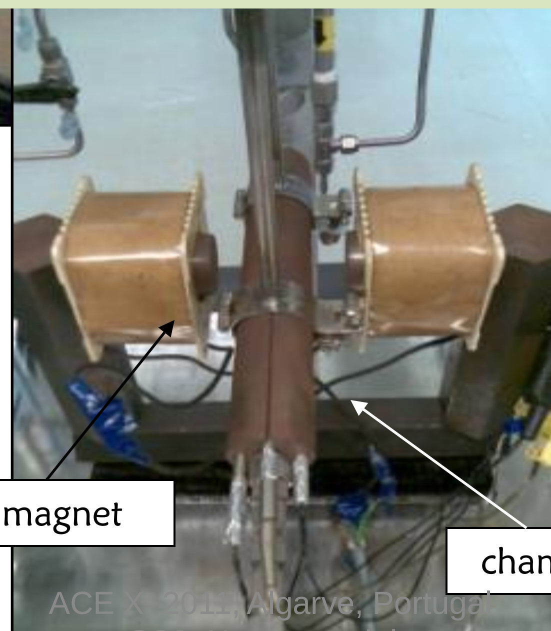
S.M. Yunusov, E.S. Kalyuzhnaya, B.L. Moroz, A.S. Ivanova, T.V. Reshtenko, L.B. Avdeeva, V.A. Likholobov, V.B. Shur, Journal of Molecular Catalysis A: Chemical, 219, 149-153, **(2004)**

NEW REACTOR DESIGN / CATALYSTS FOR AMMONIA SYNTHESIS



CATALYSTS SPINEL AND GARNET STRUCTURES

- SOL GEL
- SELF COMBUSTION
- BALL MILLING



RESULTS AND DISCUSSION

- X- RAY DIFFRACTION
- FE SEM
- HIGH RESOLUTION TEM
- TEMPERATURE PROGRAMMING REDUCTION
- MAGNETIC PROPERTIES
- AMMONIA RESULTS
- KINETIC STUDIES

Spinel (MnZn Ferrite and Garnet (Y/Sm Iron garnet)
SOL GEL (SG)

RESULTS : XRD (PHASE)

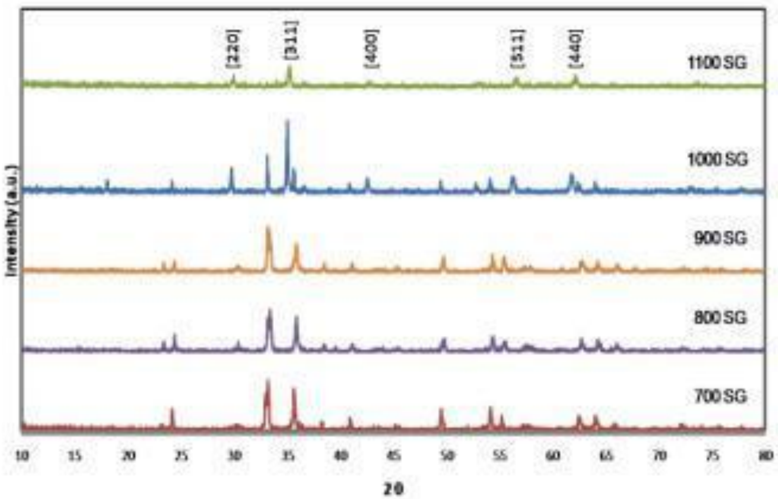


Figure 1: XRD Result for $Mn_{0.8}Zn_{0.2}Fe_2O_4$- samples prepared by sol g method

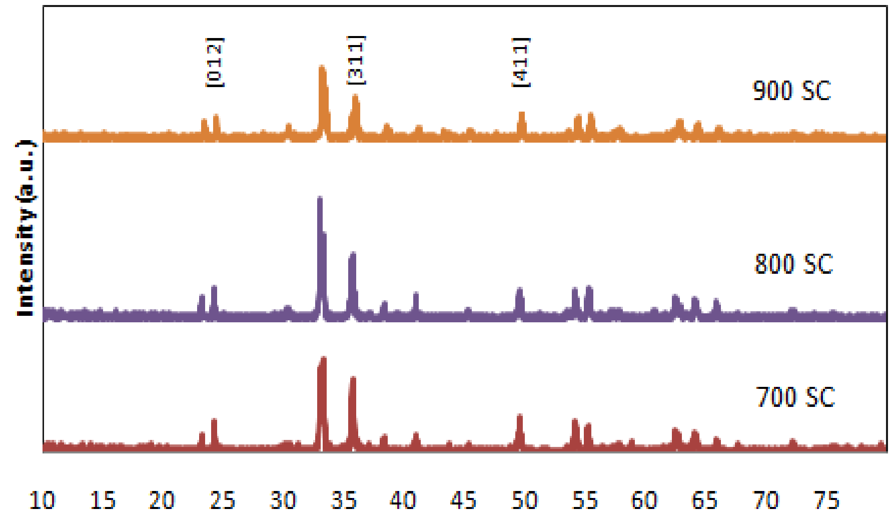


Figure 2 : XRD Result for $Mn_{0.8}Zn_{0.2}Fe_2O_4$- prepared by self combustion method

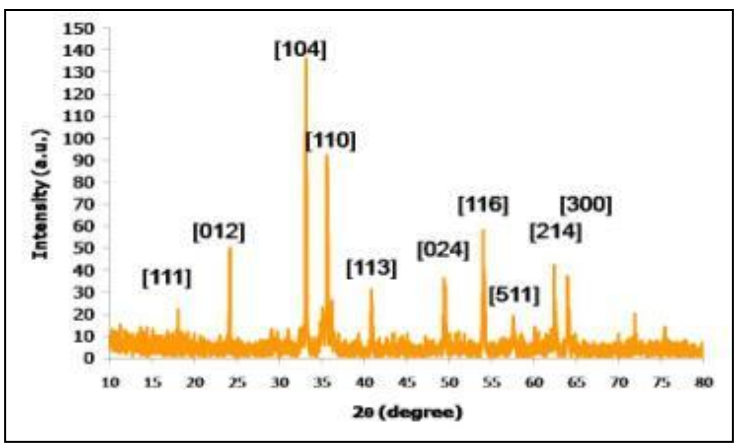


Figure 3: XRD Result for Fe_3O_4 prepared by sol gel method

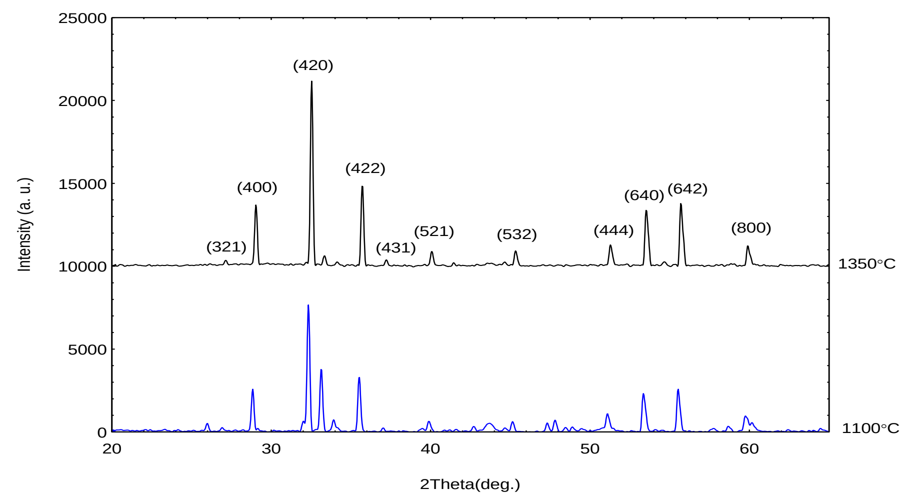
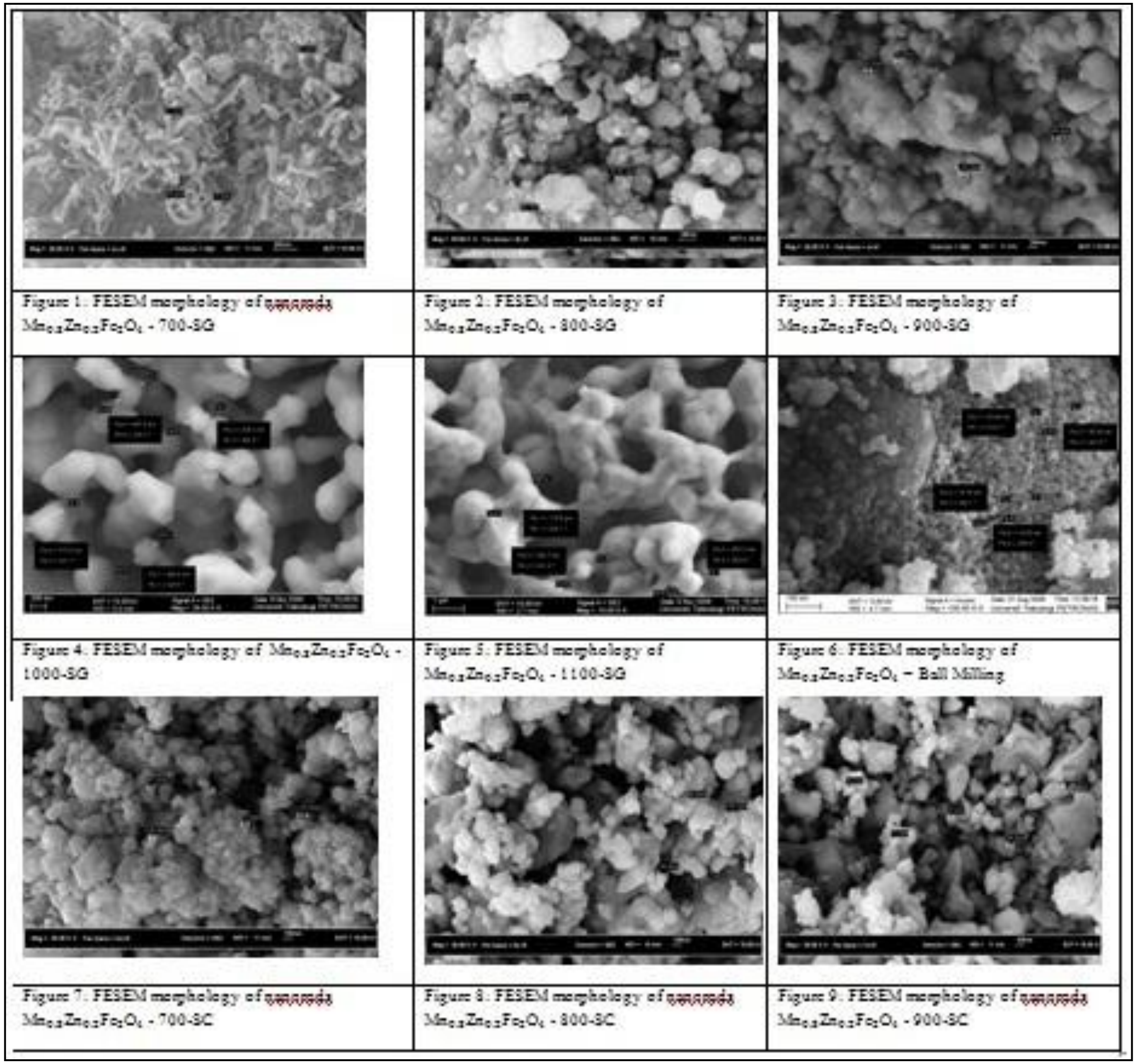


Figure 4: XRD Result for $Y_3Fe_5O_{12}$ prepared by sol gel method

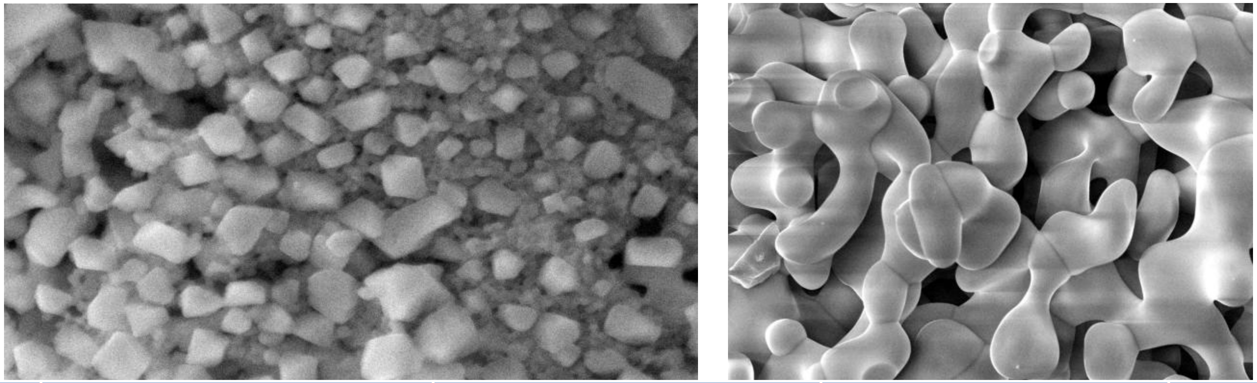
RESULTS : FESEM (Surface morphology - Spinel structure)



Sample	Average particle size (nm)
700 SG	62
800 SG	98
900 SG	125
1000 SG	417
1100 SG	554
700 SC	67
800 SC	72
900 SC	75
700 BM	20

Fig 5. Scanning electron microscopy of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ which was synthesized using sol gel (SG), self combustion (SC) and ball milling methods.

RESULTS : FESEM (Surface morphology-Garnet structure)



	Intensity (Cps)	d-spacing (Å)	FWHM (2-theta)	Crystallite Size (nm)
$Y_3Fe_5O_{12}$	285	2.80	0.14	58.4
$Sm_3Fe_5O_{12}$	411	2.76	0.13	64.8

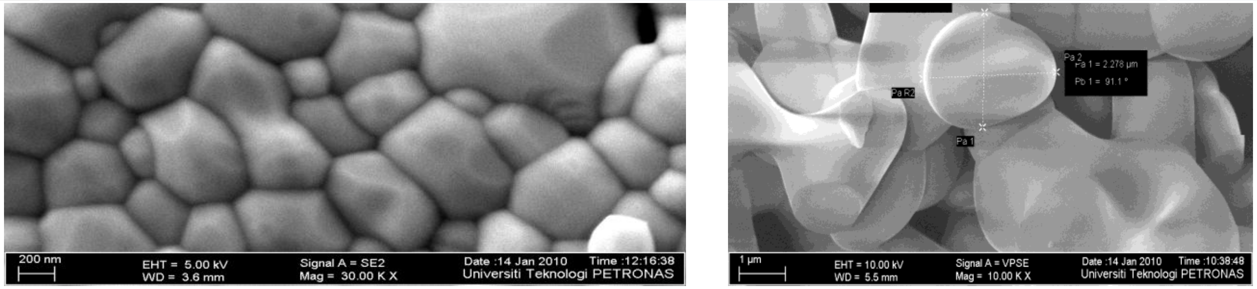


Figure 6 : (a) Yttrium iron garnet ($Y_3Fe_5O_{12}$) and (b) Samarium Iron Garnet ($Sa_3Fe_5O_{12}$) at 1350 °C

RESULTS : Electron Diffraction of Spinel - Garnet structures

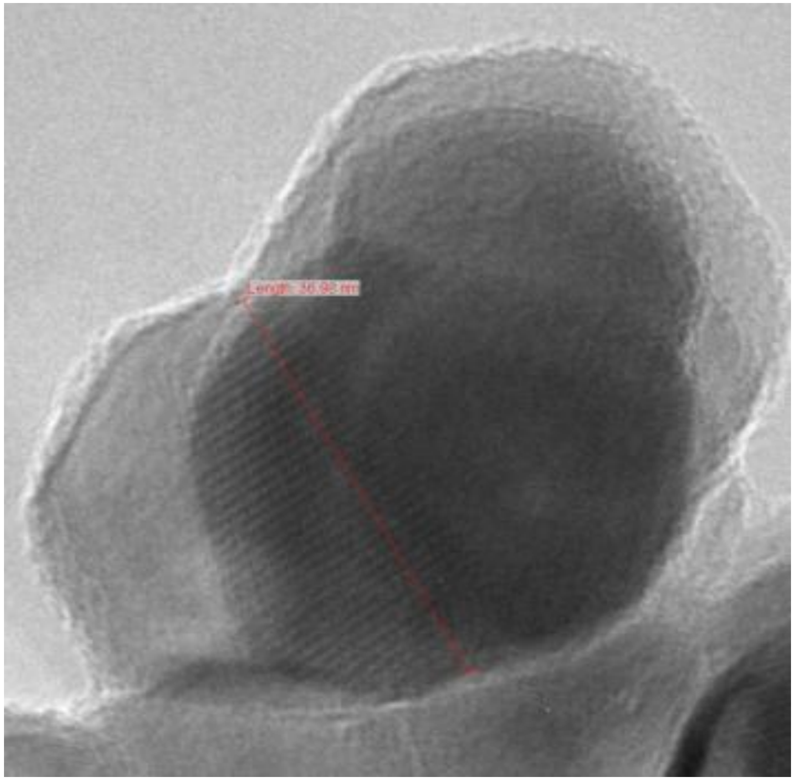


Figure 7: HRTEM image from agglomerates of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ (SG 700) sample

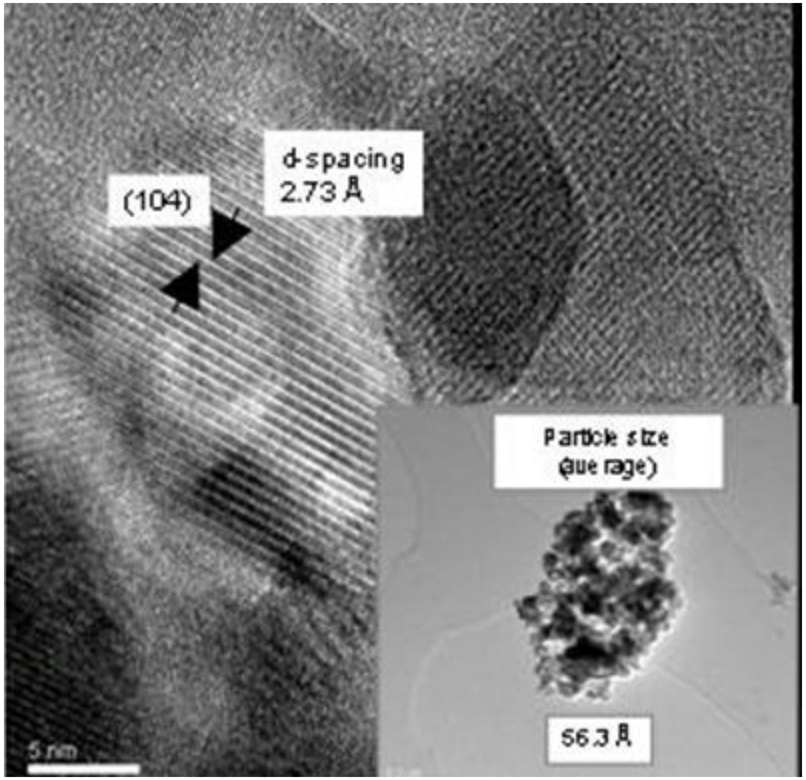


Figure 8: HRTEM image from the agglomerate of $Y_3Fe_5O_{12}$ sample.

Yahya et al., Journal of Nano Research, vol 13, 93-98, 2011.

RESULTS : Electron Diffraction of Spinel - Garnet structures

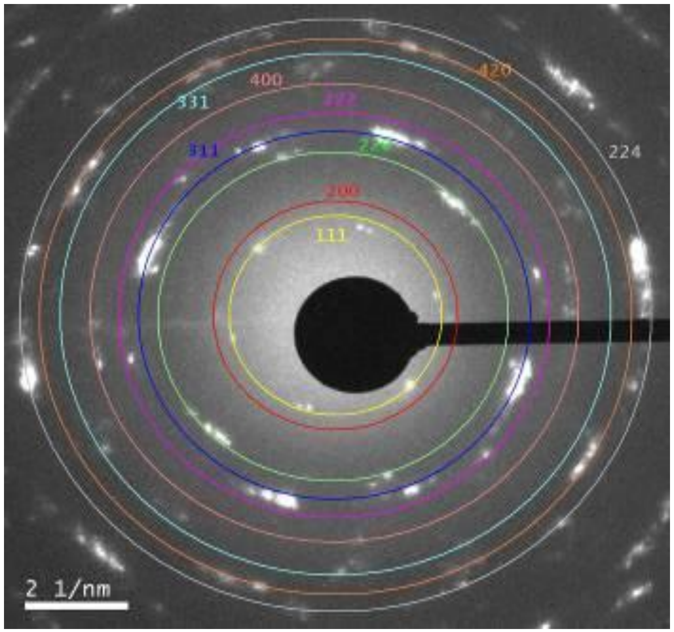


Figure 9: Diffraction pattern from agglomerate. The ring sequence corresponds to the cubic lattice of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ SG 700 sample

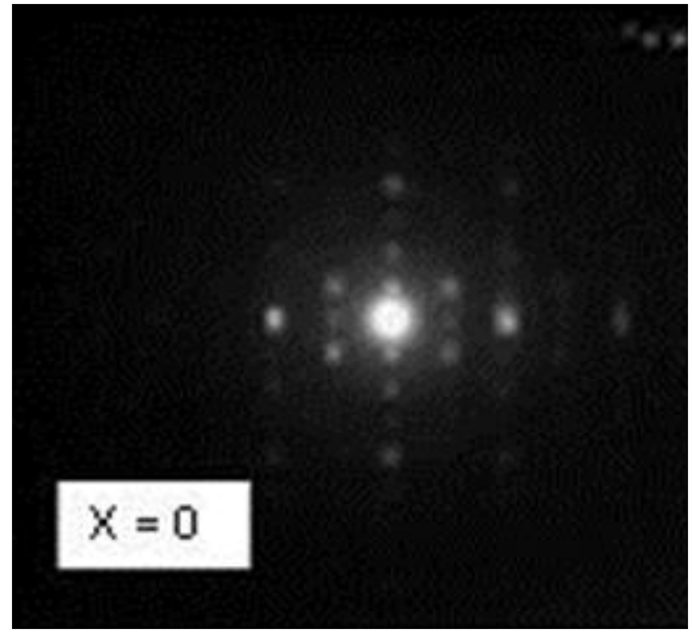
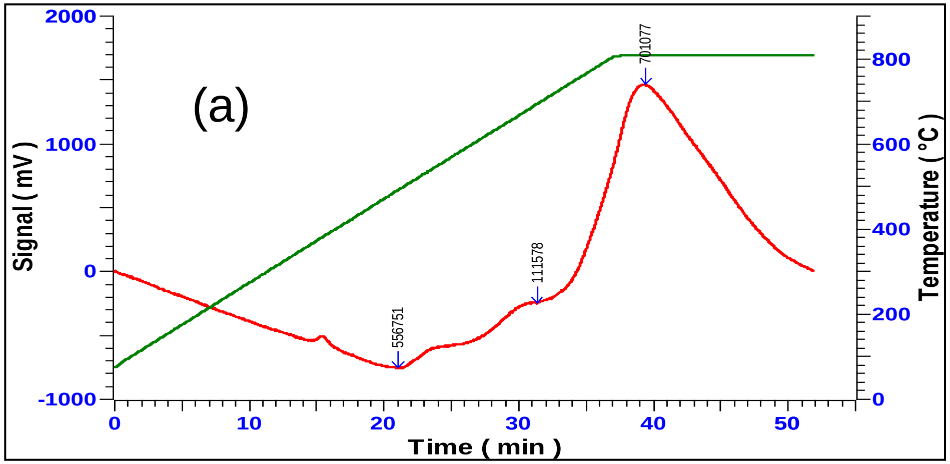
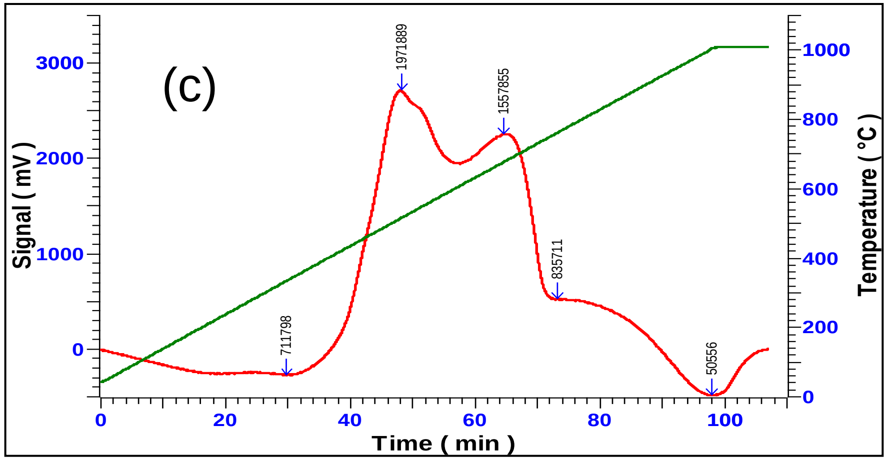


Figure 10: Diffraction pattern from the agglomerate indicating cubic structures of $Y_3Fe_5O_{12}$ sample.

Yahya et al., Journal of Nanoscience and Nanotechnology, Vol. 10. 1-5, 2010.

RESULTS : TPR of Garnet and Spinel structures





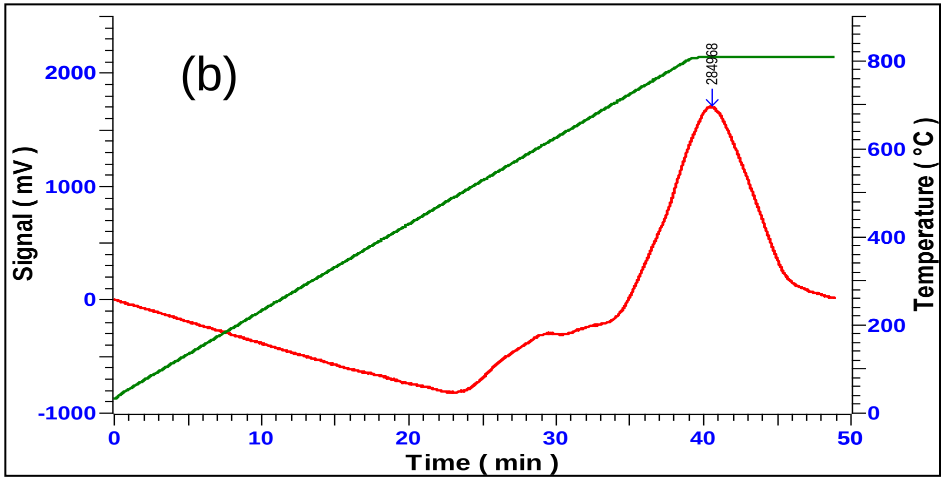


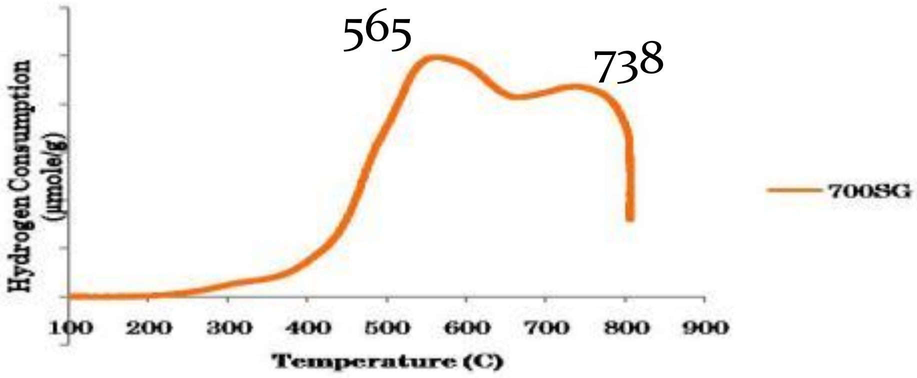
Figure 11: TPR from the agglomerates of

(a) $Y_3Fe_5O_{12}$

(b) $Sr_3Fe_5O_{12}$

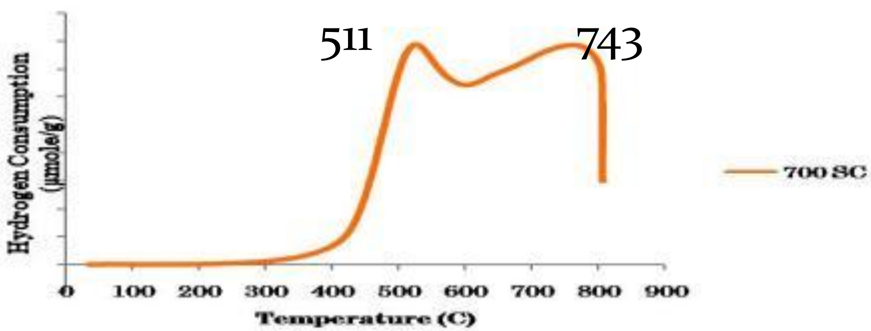
(c) $Mn_{0.8}Zn_{0.2}Fe_2O_4$

RESULTS : TPR



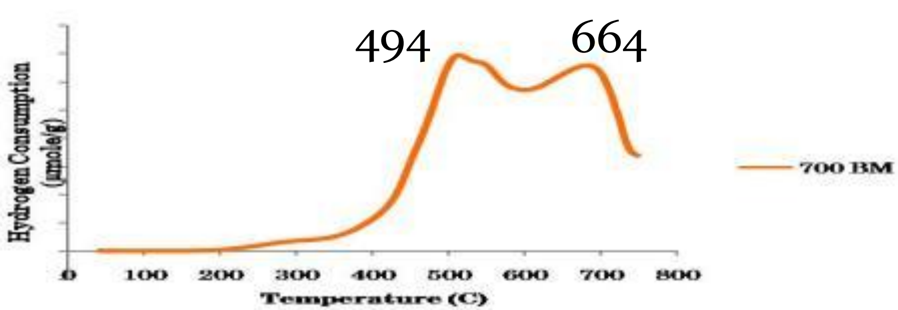
700 SG

Temperature	Reduction
565	Fe2O3 → Fe3O4
738	Fe3O4 → Fe



700 SC

Temperature	Reduction
511	Fe2O3 → Fe3O4
743	Fe3O4 → Fe

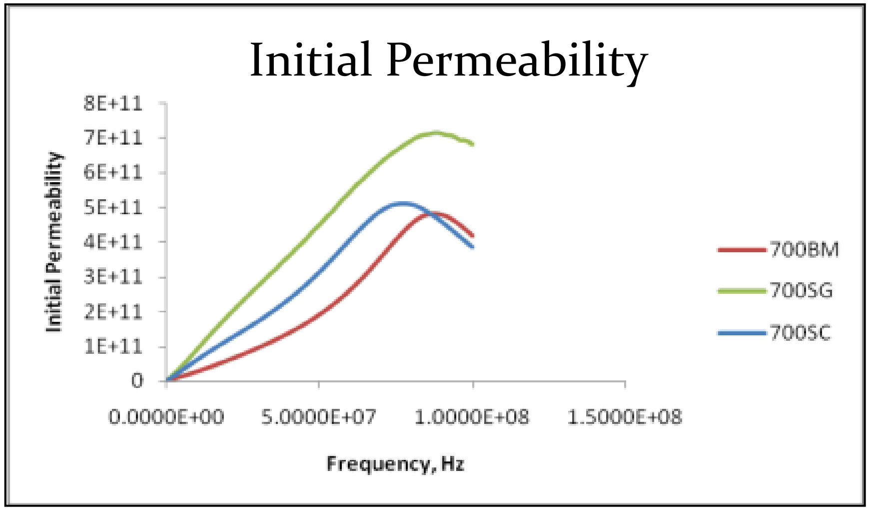


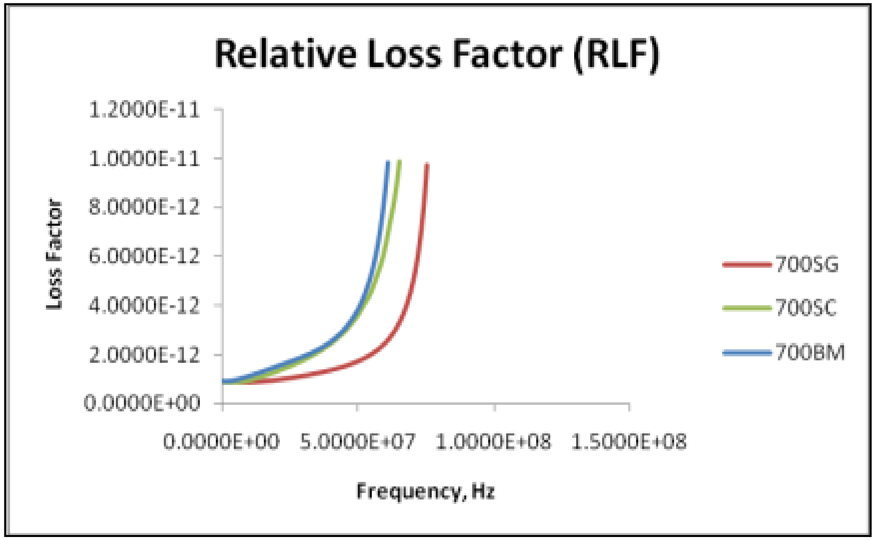
700 BM

Temperature	Reduction
494	Fe2O3 → Fe3O4
664	Fe3O4 → Fe

Figure 12: TPR from the agglomerates of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ which was prepared using sol gel, self combustion and ball milling methods.

RESULTS : MAGNETIC PROPOERTIES





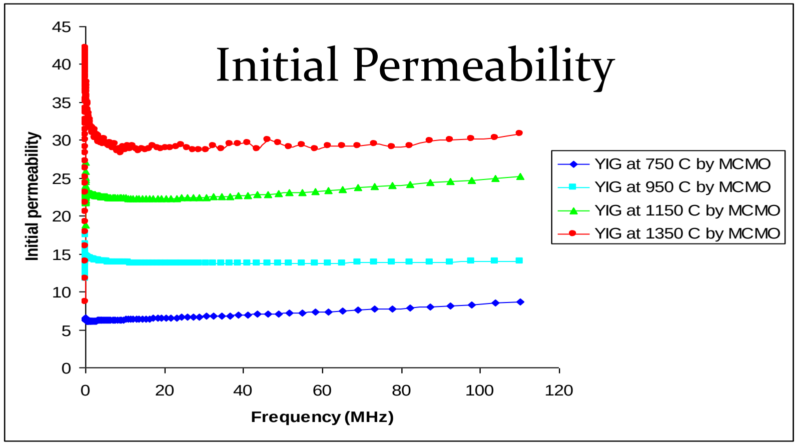
Initial permeability of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ shows that the sol gel method sample exhibits the highest value (700 SG).

Relative loss factor (RLF) of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ shows that the sol gel sample exhibits the lowest RLF (700 SG).

Figure 13: Initial permeability and relative loss factor of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ vs . frequency for the MnZn ferrite samples

RESULTS : MAGNETIC PROPOERTIES

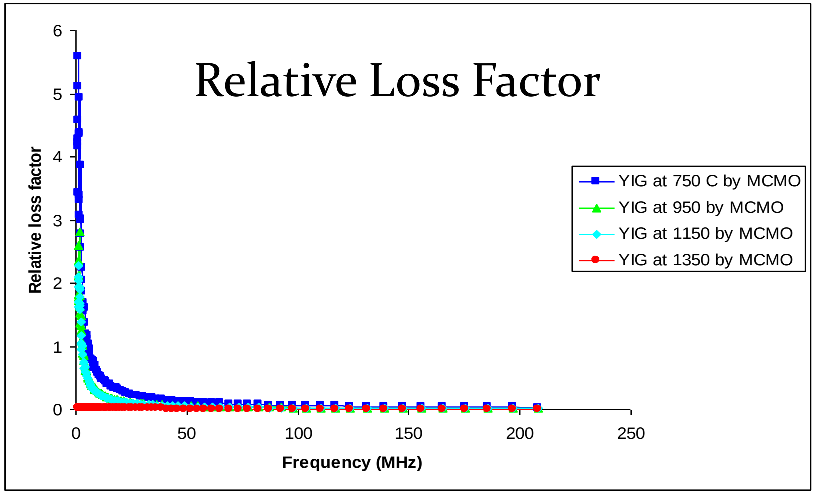
(a)



Initial permeability of Y3Fe5O12 sintered at 1350°C sample exhibits the highest value

Relative loss factor of Y3Fe5O12 sintered at 1350°C sample exhibits the lowest value

(b)



Relative loss factor of YIG at different temperatures by Sol Gel method

Figure 18: (a) Initial permeability and (b) Relative Loss Factor vs. frequency for $Y_3Fe_5O_{12}$ garnet samples

RESULTS : MAGNETIC PROPOERTIES

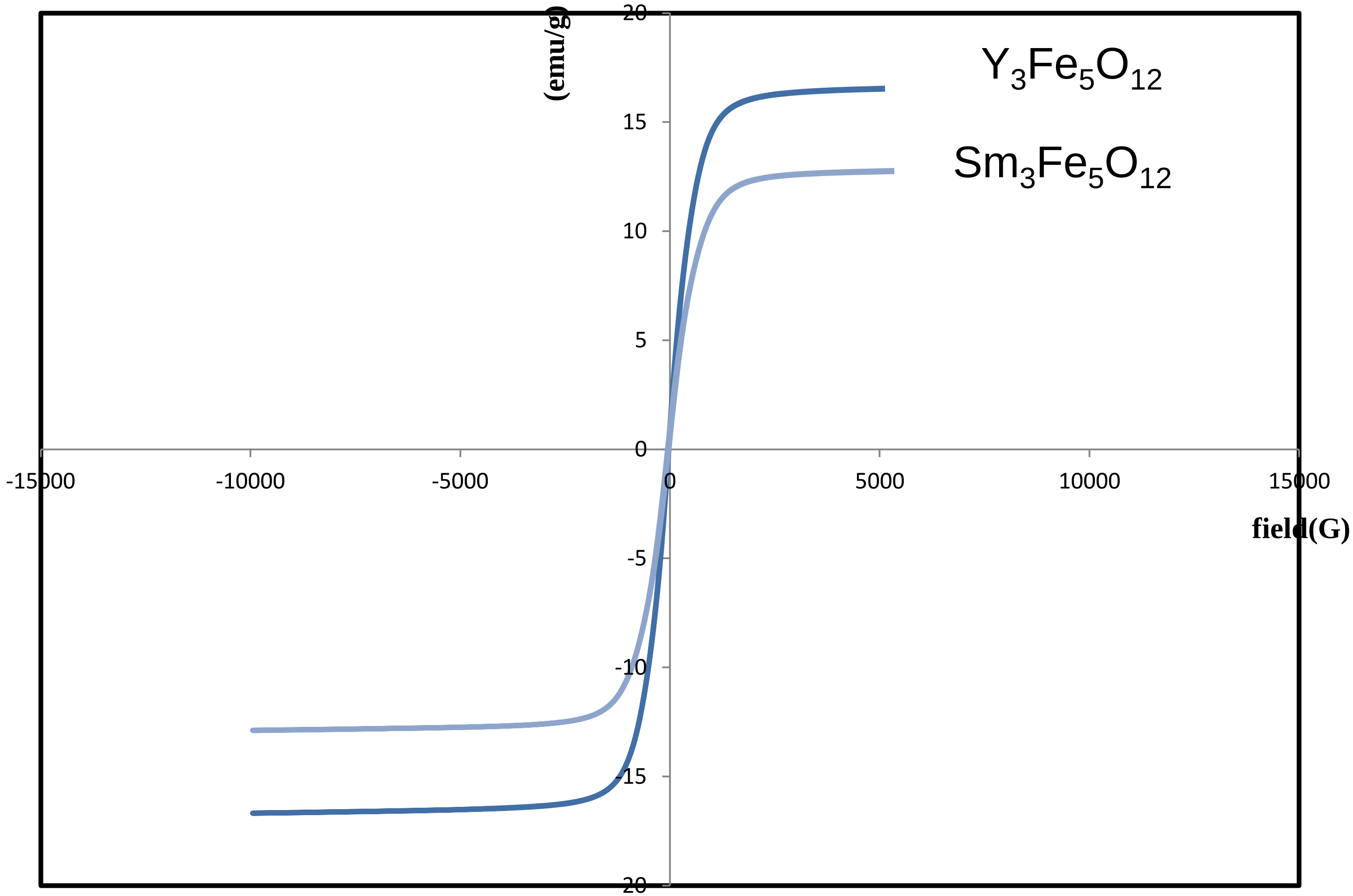
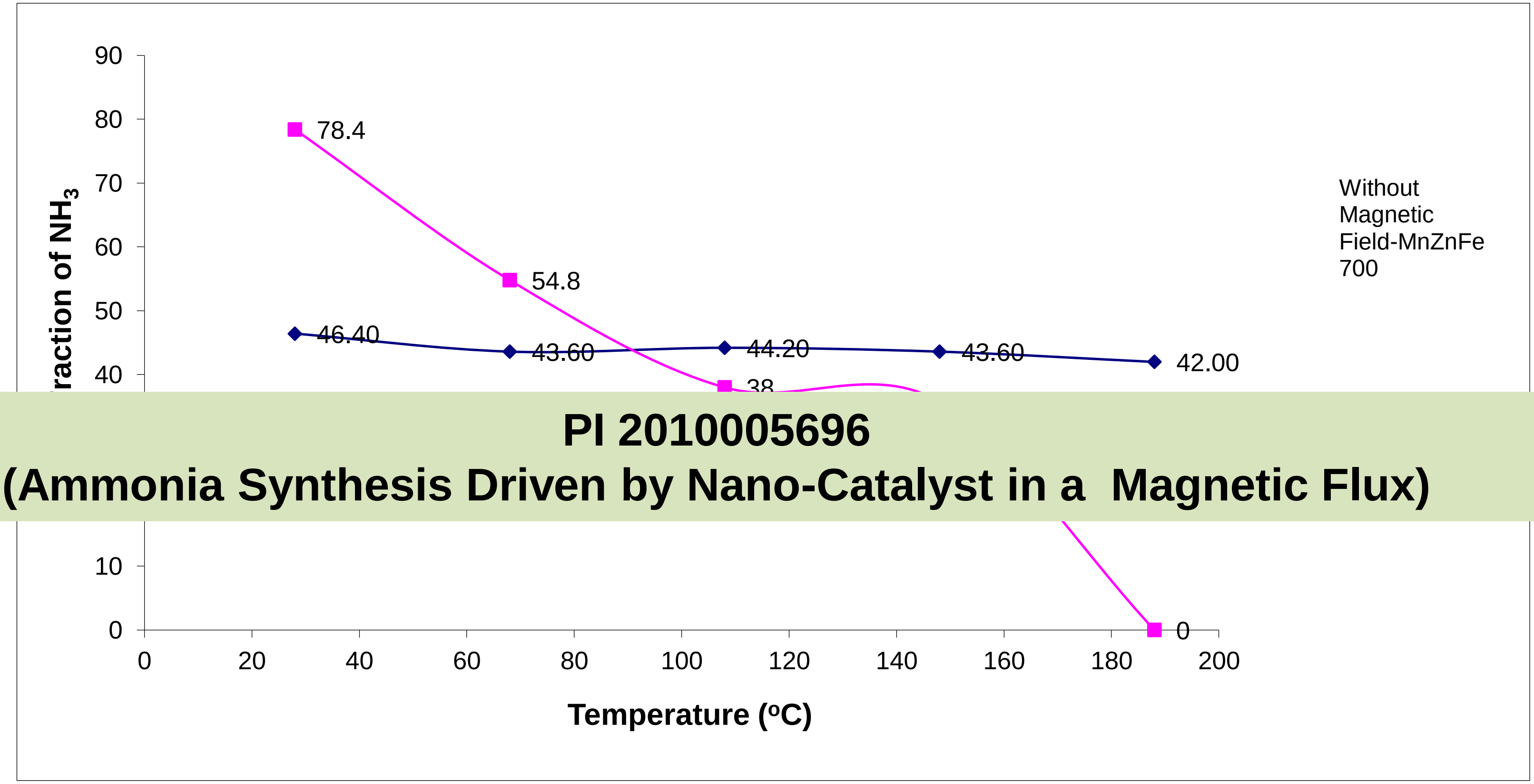


Figure 19 : VSM results of the $Y_3Fe_5O_{12}$ and $Sm_3Fe_5O_{12}$

RESULTS : AMMONIA SYNTHESIS



PI 2010005696
(Ammonia Synthesis Driven by Nano-Catalyst in a Magnetic Flux)

Figure 20 : Mole fraction of ammonia (NH-3) at different temperature shows the highest value at 28ºC with applied magnetic field

RESULTS : AMMONIA SYNTHESIS

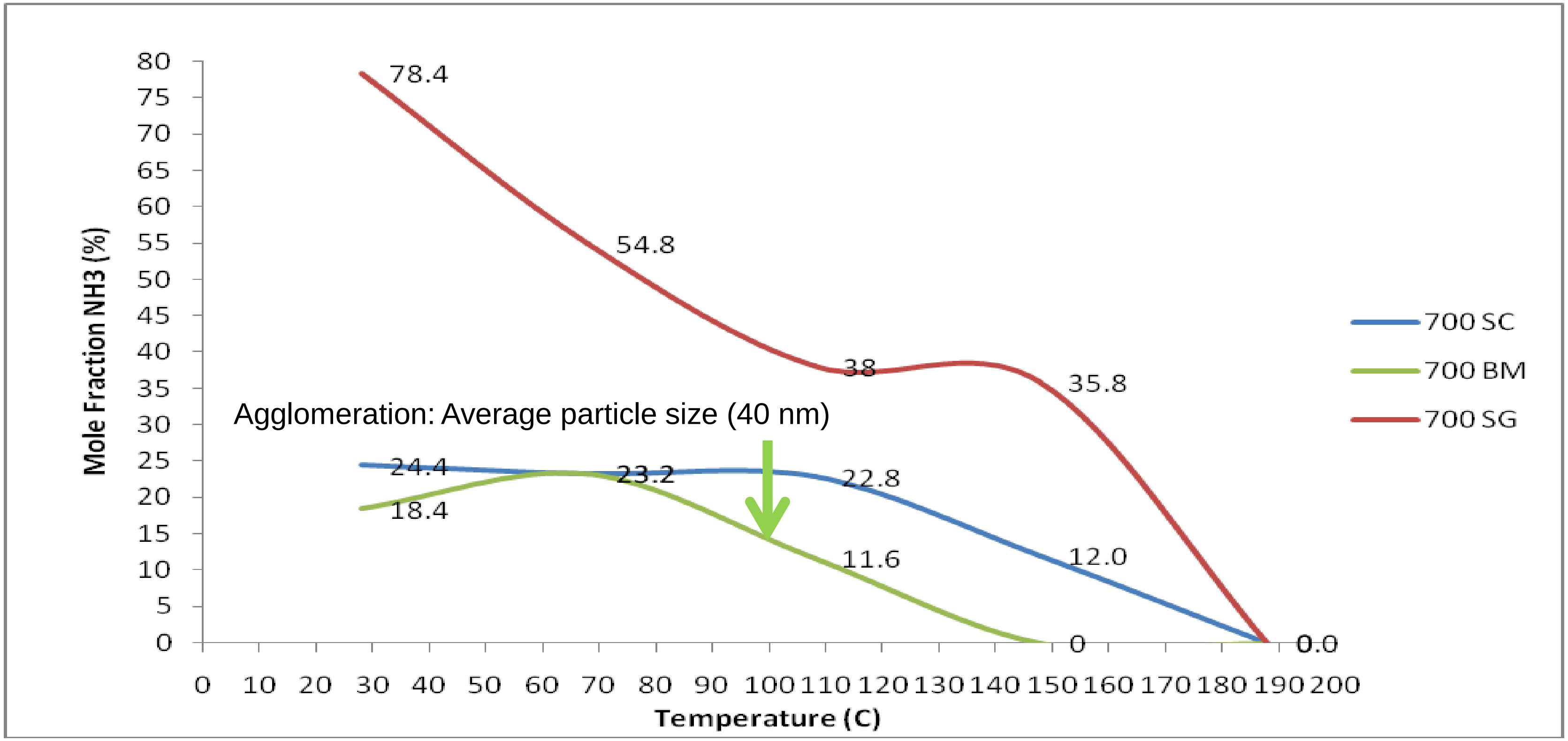


Figure 21: Mole fraction of ammonia (NH-3) using nanocatalysts with sol gel, self combustion and ball milling preparation methods (the ammonia highest value is shown at 28ºC by using $Mn_{0.8}Zn_{0.2}Fe_2O_4$ -700 SG as nanocatalyst

RESULTS : AMMONIA SYNTHESIS

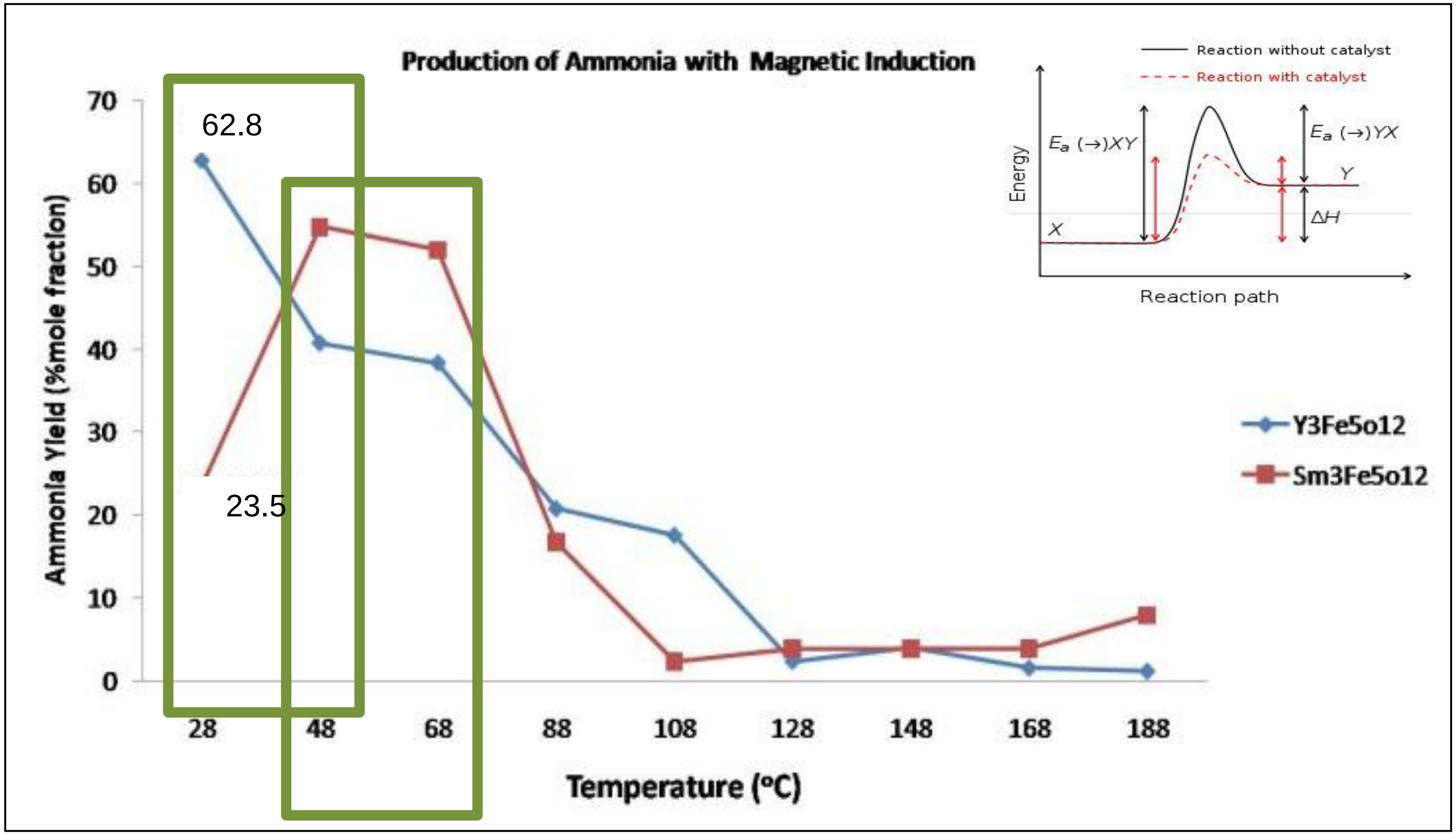
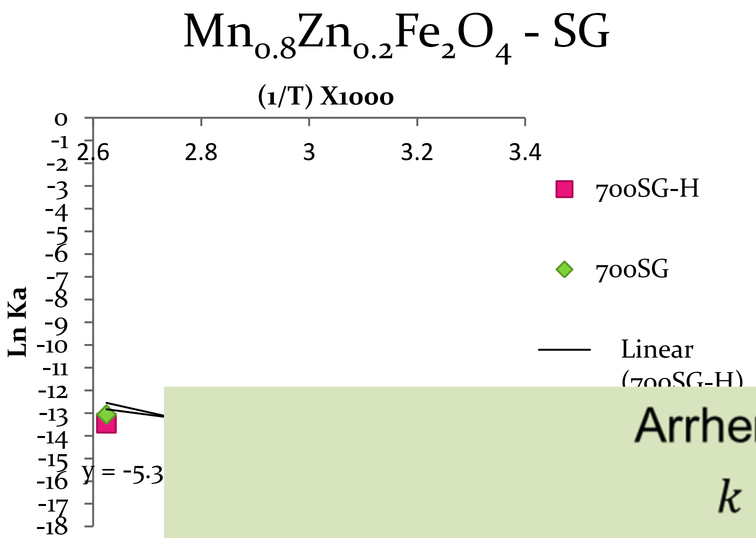
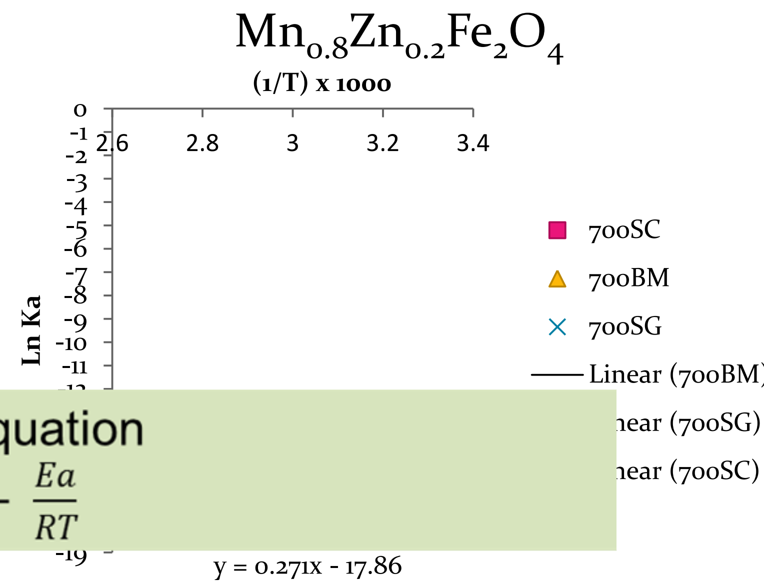


Figure 22: Mole fraction of ammonia (NH-3) at different temperature shows the highest value at 28°C by using $Y_3Fe_5O_{12}$ and $Sm_3Fe_5O_{12}$ as nanocatalysts

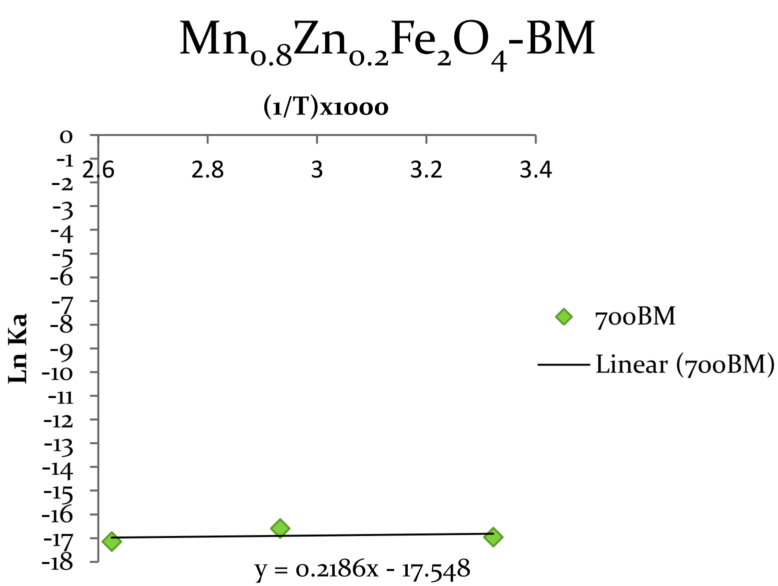
RESULTS : Activation Energy of $MnZnFe_2O_4$

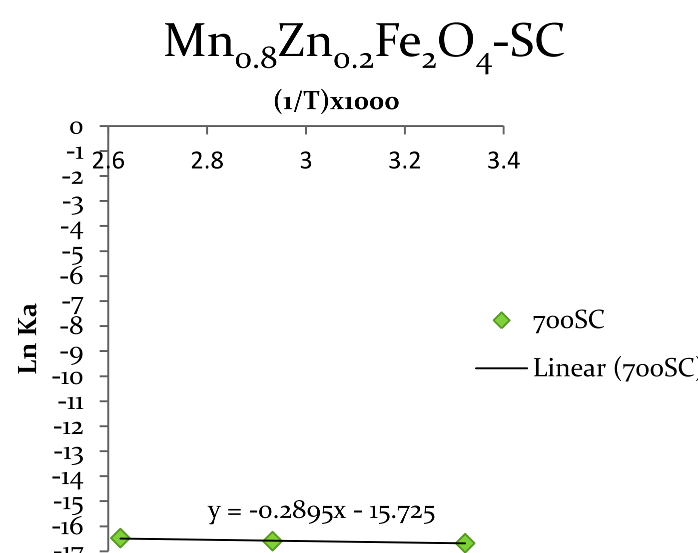




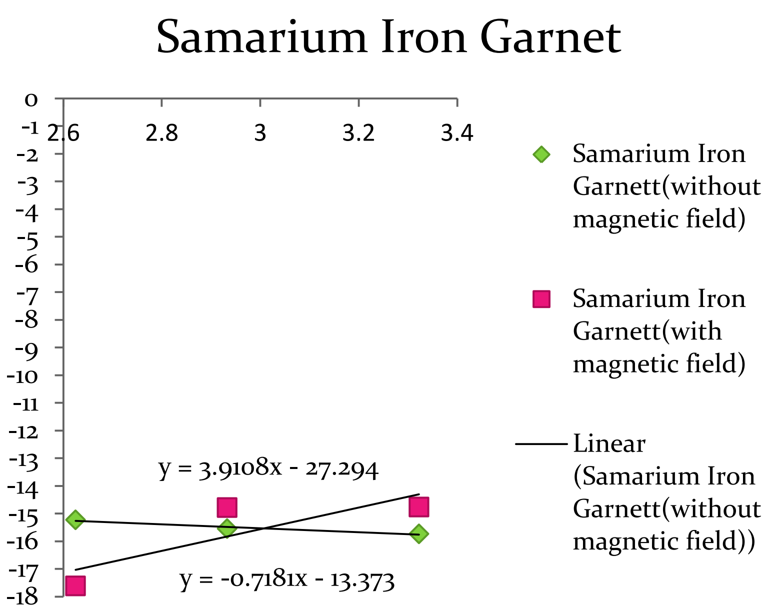
Arrhenius equation

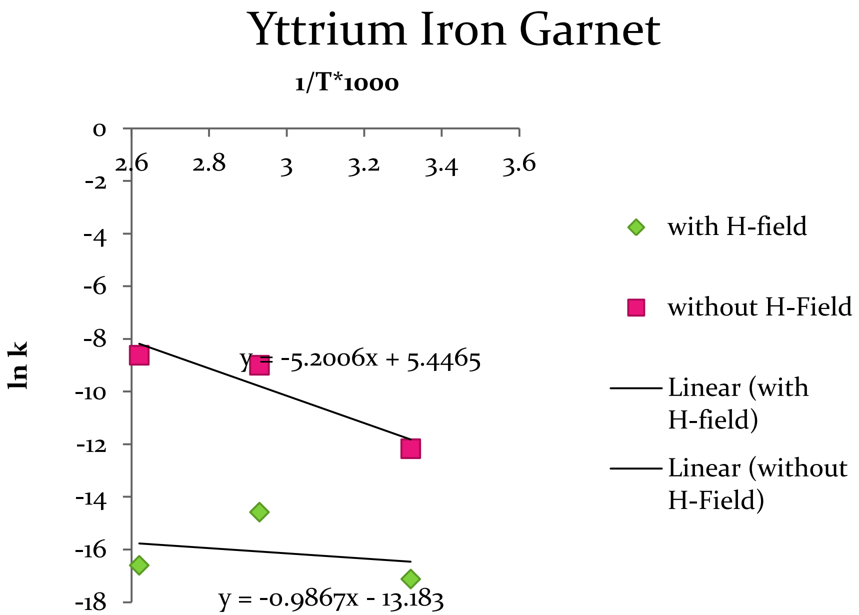
$$k = Ae - \frac{Ea}{RT}$$





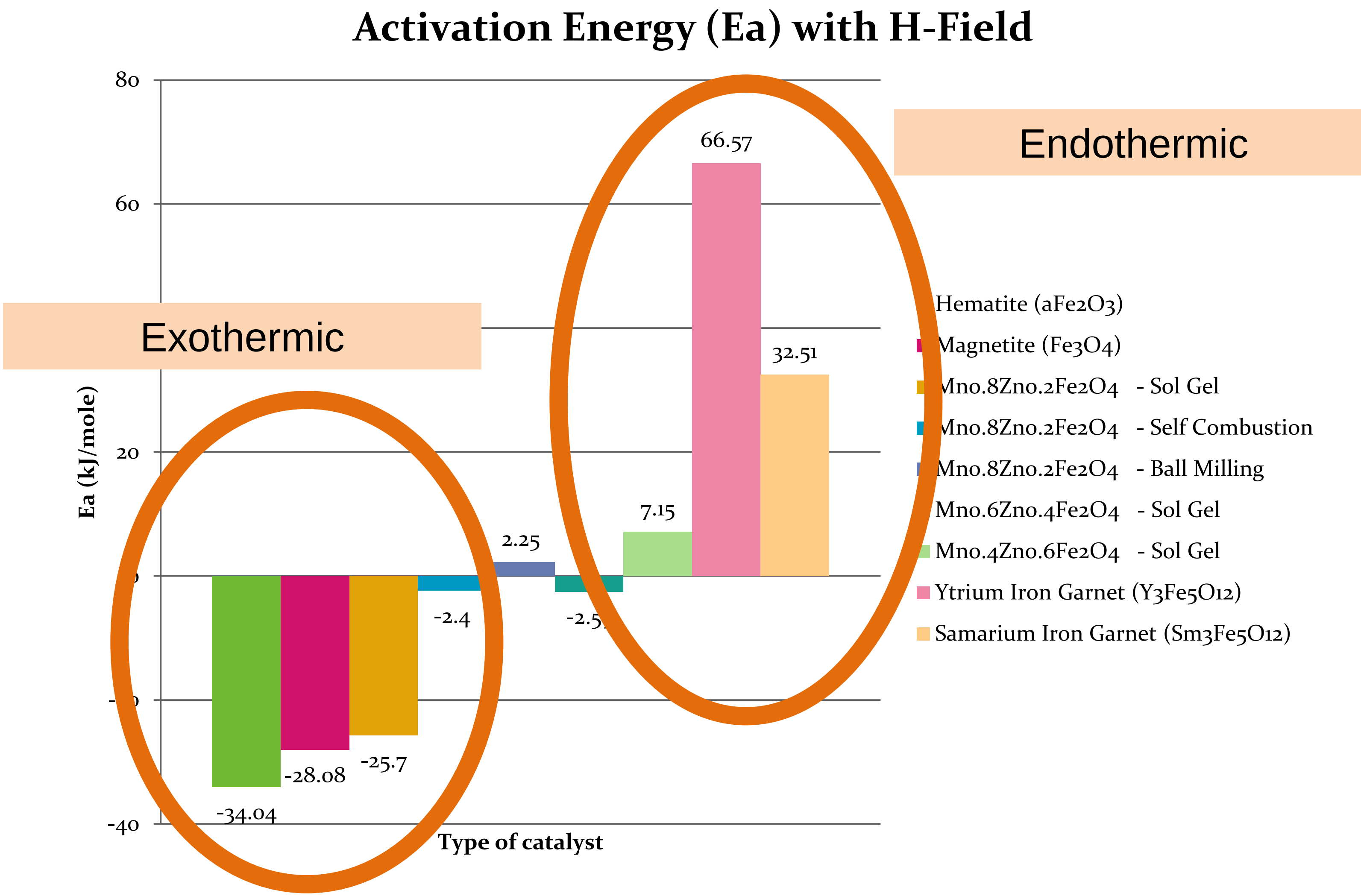
RESULTS : Activation Energy of $MnZnFe_2O_4$





Sample	Activation Energy (kJ/mole)	
	H-field	No H-field
$Y_3Fe_5O_{12}$	66.57	11.87
$Sm_3Fe_5O_{12}$	31.34	-9.17

Activation Energy (Ea) with H-Field



SUMMARY

Material	Ea (kJ/ mole)		Yield ($x10^{-3}$ mole.gcat^{-1}.h^{-1})
	With H-field	Without H-field	With H-field
Hematite (αFe_2O_3)	-34.04	-96.49	7.70
Magnetite (Fe_3O_4)	-28.08	-	8.81
$Mn_{0.8}Zn_{0.2}Fe_2O_4$ - Sol Gel	-25.7	-44.16	3.92
$Mn_{0.8}Zn_{0.2}Fe_2O_4$ - Self Combustion	-2.40	-44.16	3.61
$Mn_{0.8}Zn_{0.2}Fe_2O_4$ - Ball Milling	2.25	-44.16	3.46
$Mn_{0.6}Zn_{0.4}Fe_2O_4$ - Sol Gel	-2.57	5.75	1.57
$Mn_{0.4}Zn_{0.6}Fe_2O_4$ - Sol Gel	7.15	3.07	3.68
Ytrium Iron Garnet ($Y_3Fe_5O_{12}$)	66.57	11.87	5.57
Samarium Iron Garnet ($Sm_3Fe_5O_{12}$)	32.51	-5.97	2.31

Summary:

• Ferrite and Iron oxide nanocatalyst obtain the exothermic reaction by the presence of magnetic field.

•Garnets (YIG and SaIG) obtain an endothermic reaction for both condition, with or without the presence of magnetic field.

•Ferrite and Iron oxide nanocatalysts show decreasing activation energy with the presence of magnetic field.

•Garnets show the increase of activation energy by the presence of magnetic field.

CONCLUSION : OPTIMUM CONDITION

- Ammonia synthesis has been successfully achieved. The yield was 76% increasing by using MAGNETIC INDUCTION METHOD.

Optimum condition in this system:

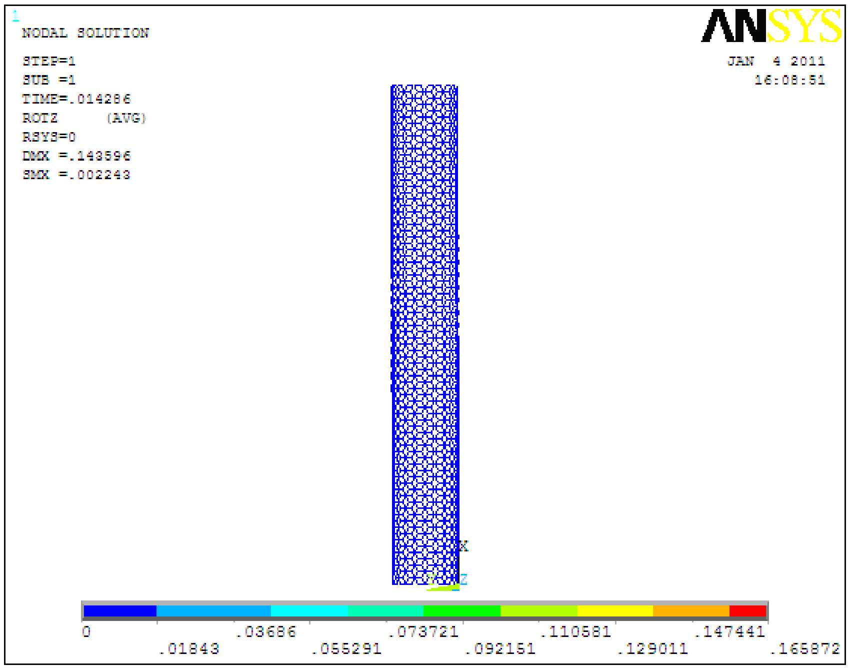
- (1) $Mn_{0.8}Zn_{0.2}Fe_2O_4$ and $Y_3Fe_5O_{12}$ as nanocatalysts
- (2) Room temperature (28^0C)
- (3) Ambient pressure (1.01 bar)
- (4) Magnetic field strength (1T)

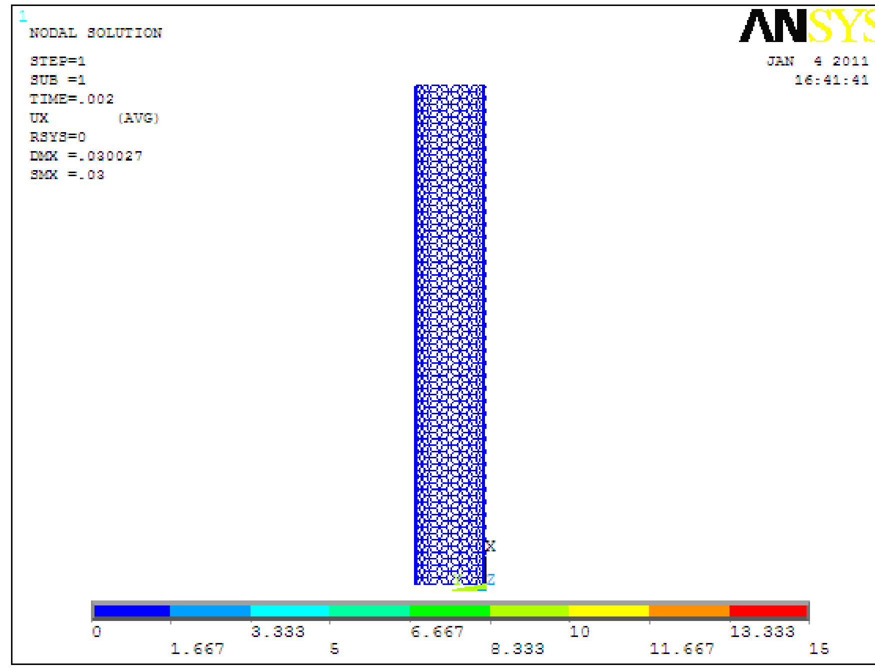
WAY FORWARD

- GARNET STRUCTURES
- LOW TEMPERATURE
- MAGNETO-THERMO DYNAMICS
- HYSTERESIS
- CURIE TEMPERATURE
- KINETIC STUDIES

Finite Element Method for catalyst support strenght

Finite Element Method : Support Strength





Shear modulus= 0.327 TPa

Young's modulus= 2.037 TPa

ACHIEVEMENTS

Awards:

- Gold Medal for IENA Germany 2010

- Gold Medal for ITEX 2010

- Russian Best Invention Award

ACHIEVEMENTS

- Gold Medal at 25th EDX 2010

- Gold Medal at 26th EDX 2010
- Best Presenter Award at 26th EDX 2010
- 1ST Runner Up for Most Innovative Award at 26th EDX 2010

ACHIEVEMENTS

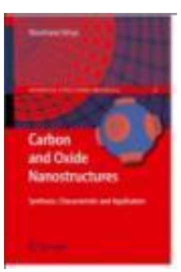
PUBLICATIONS

International Journals:

- Yahya N, Puspitasari P, Koziol K, Zabidi NA, Othman MF. International Journal of Engineering, vol.10, 01, pp. 95-100. (2010)
- Puspitasari P, Yahya N, Zabidi NA, Ahmad NA. International Journal of Applied Sciences. (2010)
- Ahmad NA, Yahya N, Zakariah MH, Puspitasari P. AIP Conf. Proc 1136, pp. 406-413. (2009)
- Yahya N, Zahari SN, Ramli A, Mohamad NM, Puspitasari P, Che Zul N. AIP Conf. Proc 1136, pp. 401-405. (2009)
- Yahya N, Daud H, Tajuddin NA, Mohd Daud H, Shafie A, Puspitasari P. Journal of Nanoresearch. Vol. 11, 01. pp 25-34. (2010)

Book Chapter:

- Yahya N, Puspitasari P., Koziol K, Guiseppe P. Chapter 17: Ammonia Synthesis. Carbon and Oxide Nanostructured. Springer. (2010)



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- ACCELRYS SOFTWARE
- CST SOFTWARE

THANK YOU